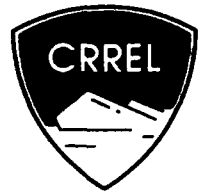


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Effect of Concentration on Sorption of Dissolved Organics by Well Casings

Louise V. Parker and Thomas A. Ranney

May 1993

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Abstract

This report examines sorption of low ppb levels of organic solutions by polytetrafluoroethylene (PTFE), rigid polyvinyl chloride (PVC) and stainless steel 304 and 316 well casings. Nineteen organics that were either on the EPA priority pollutant list or of concern to the U.S. Army were selected, including several munitions and chlorinated solvents. These compounds were selected to give a range in physical properties such as solubility in water, octanol-water partition coefficient and molecular structure. When these results were compared with the results from a similar study conducted at ppm levels, the rate and extent of sorption by PTFE and PVC was the same for almost all analytes. There were no losses of any compounds associated with stainless steel. At these low levels (ppm and ppb) the rate of diffusion within the polymer (PVC and PTFE) is independent of concentration. Only with PTFE are the rates rapid enough to be of concern when monitoring for some compounds in groundwater. Tetrachloroethylene was the compound sorbed by PTFE the most rapidly. The study showed that PVC well casings are suitable for monitoring low levels (ppm and ppb) of organics.

For conversion of SI metric units to U.S./British customary units of measurement consult *Standard Practice for Use of the International System of Units (SI)*, ASTM Standard E380-89a, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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Special Report 93-8



**US Army Corps
of Engineers**

Cold Regions Research &
Engineering Laboratory

Effect of Concentration on Sorption of Dissolved Organics by Well Casings

Louise V. Parker and Thomas A. Ranney

May 1993

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PREFACE

This report was prepared by Louise V. Parker, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory, and Thomas A. Ranney, Summer Associate of the Army Research Office High School Faculty Program. Funding was provided by the U.S. Army Environmental Center (formerly the Toxic and Hazardous Materials Agency [USATHAMA]), Martin H. Stutz, Project Monitor.

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This publication reflects the personal views of the authors and does not suggest or reflect the policy, practices, programs, or doctrine of the U.S. Army or Government of the United States. The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of the use of such commercial products.

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Effect of Concentration on Sorption of Dissolved Organics by Well Casings

LOUISE V. PARKER and THOMAS A. RANNEY

INTRODUCTION

Parker (1992) reviewed the literature available on the sorption of organics in aqueous solution by three commonly used well casing materials: polytetrafluoroethylene (PTFE), rigid polyvinyl chloride (PVC) and stainless steel (SS). She concluded that in laboratory studies conducted under sterile conditions (Gillham and O'Hannesin 1990, Parker et al. 1990), polymeric materials such as rigid PVC and PTFE sorb many organics while stainless steel does not (Table 1). Furthermore, PTFE tends to sorb organics at a faster rate and to a greater extent than rigid PVC. While the results from a study by Reynolds and Gillham (1986) show that sorption

was not always greater for PTFE than for PVC, losses due to biodegradation cannot be ruled out in this study since nothing was done to prevent this from occurring. In fact, there is evidence that biotransformation occurred in the samples exposed to PVC. After three weeks the authors noticed that these samples contained several additional peaks that were similar to peaks observed in degraded stock solutions of the organics (bromoform and hexachloroethane).

Gillham and O'Hannesin (1990) noted that the rate of sorption increases with increasing hydrophobicity of the organics. For PTFE we (Parker et al. 1990) were able to correlate losses with the compound's octanol-water partition coefficient (K_{ow}).

Table 1. Time for 10% loss of dissolved organics (hours).

| Compound | PTFE | PVC | SS | Data source |
|------------------------------------|---------|----------|--------|-------------------------------|
| Benzene | 24-48 | 48-96 | > 1344 | Gillham and O'Hannesin (1990) |
| Toluene | 3-6 | 24-48 | > 1344 | Gillham and O'Hannesin (1990) |
| Ethylbenzene | 1-3 | 12-24 | > 1344 | Gillham and O'Hannesin (1990) |
| <i>m</i> -xylene | 3-6 | 12-24 | > 1344 | Gillham and O'Hannesin (1990) |
| <i>o</i> -xylene | 6-12 | 12-24 | > 1344 | Gillham and O'Hannesin (1990) |
| <i>p</i> -xylene | 1-3 | 12-24 | > 1344 | Gillham and O'Hannesin (1990) |
| RDX | > 1000 | > 1000 | > 1000 | Parker et al. (1990) |
| Trinitrobenzene | > 1000 | > 1000 | > 1000 | Parker et al. (1990) |
| <i>cis</i> -1,2-dichloroethylene | 168 | 1000 | > 1000 | Parker et al. (1990) |
| <i>trans</i> -1,2-dichloroethylene | 8-24 | >24-72 | > 1000 | Parker et al. (1990) |
| <i>m</i> -nitrotoluene | 168 | > 1000 | > 1000 | Parker et al. (1990) |
| Trichloroethylene | 8 | 168-1000 | > 1000 | Parker et al. (1990) |
| Chlorobenzene | 24 | 168-1000 | > 1000 | Parker et al. (1990) |
| <i>o</i> -dichlorobenzene | 8-24 | 168-1000 | > 1000 | Parker et al. (1990) |
| <i>p</i> -dichlorobenzene | 1-8 | 72 | > 1000 | Parker et al. (1990) |
| <i>m</i> -dichlorobenzene | 1-8 | ~72 | > 1000 | Reynolds and Gillham (1986) |
| 1,1,1-trichloroethane | ~24 | > 840 | | Reynolds and Gillham (1986) |
| 1,1,2,2-tetrachloroethane | ~336 | ~ 336 | | Reynolds and Gillham (1986) |
| Bromoform | > 840 | 72 | | Reynolds and Gillham (1986) |
| Hexachloroethane | ~24 | ~ 24 | | Reynolds and Gillham (1986) |
| Tetrachloroethylene | < 0.08* | 24 | | Reynolds and Gillham (1986) |

* Less than five minutes.

In all of the previous studies, losses were attributed to absorption within the polymer matrix. Absorption of organics by polymers is described as a two-step process involving first sorption and dissolution into the polymer surface followed by diffusion into the polymer matrix (Serota et al. 1972, Yasuda and Stannett 1975, Reynolds and Gillham 1986). Reynolds and Gillham (1986) developed an analytical model based on Fick's second law of diffusion of organics in pipe to account for the decrease in the relative concentration (solution concentration divided by the initial concentration) with time:

$$\frac{C}{C_0} = \exp\left[\frac{KDt}{A^2}\right] \operatorname{erfc}\left[\frac{(KDt)^{1/2}}{A}\right] \quad (1)$$

where C = concentration in solution

C_0 = initial concentration

K = partition coefficient between the organic in solution and the polymer (dimensionless)

D = diffusion coefficient (cm^2/s)

A = ratio of solution volume to polymer surface area (cm)

t = time (s)

erfc = error function.

Reynolds and Gillham (1986) and Gillham and O'Hannesin (1990) found reasonably good agreement between this diffusion model and their data. They felt that this suggested that sorption by rigid PVC and PTFE involves diffusion through the polymer material. They noted that one implication of this was that the sorption capacity of polymeric materials should not be significantly reduced by saturation of surface sorption sites as would occur with adsorption. Instead, diffusion into the polymer matrix should continue to replenish sites for sorption until the polymer is saturated. In our studies (Parker et al. 1990) we noted that the rate of sorption appeared to be first order, and we predicted that the relative concentration should be independent of the initial concentration (Castellan 1964). Thus, the percent loss at a given time should be independent of concentration; Reynolds and Gillham (1986) made a similar prediction.

This study was conducted to address concerns by regulatory agencies regarding losses at low ppb (or near detection) levels and to determine if in fact sorption is independent of concentration at the ppb and ppm levels. This study attempts to duplicate our previous study (Parker et al. 1990) using mixed solutions of the same organics used previ-

ously, except at a lower concentration (approximately 20 ppb vs 2 ppm used in the previous study).^{*} Compounds tested include hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); 1,3,5-trinitrobenzene (TNB); *cis*- and *trans*-1,2-dichloroethylene (CDCE and TDCE); *m*-nitrotoluene (MNT); trichloroethylene (TCE); chlorobenzene (CLB); and *o*- and *m*-dichlorobenzene (ODCB and MDCB). One other compound, *p*-dichlorobenzene (PDCB), was used in the previous study but was not used in this study because it made the analysis time too long and because losses of this compound were equivalent to those seen with MDCB. These compounds were selected because they were either on the EPA list of priority pollutants or of concern to the U.S. Army. Additional criteria used in selecting these compounds included their molecular structure, solubility in water, K_{ow} value and retention time (using RP-HPLC). However, because we were working close to the detection levels for many of these compounds, the same HPLC method that was used in the ppm study could not be used for all the compounds. Thus, for analytical reasons this study was conducted as three separate experiments, and several additional compounds were included. Additional compounds included several other munitions and their degradation products: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); 1,3-dinitrobenzene (DNB); nitrobenzene (NB); 2,4,6-trinitrotoluene (TNT); 2-amino-4,6-dinitrotoluene (2AmDNT); 2,4-dinitrotoluene (DNT); and *o*-, *p*- and *m*-nitrotoluene (ONT, PNT and MNT). Two other volatiles were also tested: benzene (BENZ) and tetrachloroethylene (PCE). PCE was selected because the study of Reynolds and Gillham (1986) found that PTFE sorbs this compound the most rapidly of all compounds studied to date.

MATERIALS AND METHODS

Four types of 5-cm- (2-in.-) diameter well casings manufactured specifically for groundwater monitoring were used in this study: schedule 40 PVC, PTFE, and 304 and 316 stainless steel. Sections were cut to a length of 11–14 mm and then cut into quarters. The lengths were varied so that the final surface areas would be constant. Special care was taken to eliminate contamination from grease or oil in the cutting process. All the pieces were placed in solutions of detergent and deionized

^{*} The previous study will be referred to as the ppm study; the current study will be called the ppb study.

water and sonicated for 10 minutes, then rinsed several times with deionized water to remove the detergent, sonicated for 20 minutes in fresh deionized water, and then left to air dry. Two pieces of the same casing material were placed in individual 40-mL borosilicate glass vials that were then filled with the aqueous test solution so that there was no headspace; they were capped with Teflon-lined plastic caps. Vials with test solution but no well casing material served as controls, allowing us to eliminate any effects such as those that might be due to the vials or caps. The ratio of casing surface area to solution volume was $0.79 \text{ cm}^2/\text{mL}$, and the ratio of solution volume to volume of casing material was approximately 10:1. Separate vials were used for each sampling period so that the test solution could be discarded after sampling. For each material and time, there were four replicates in the first experiment and three replicates in the last two experiments.

The first experiment investigated the sorption of HMX, RDX, TNB, DNB, NB, TNT, 2AmDNT, DNT, ONT, PNT and MNT. The second experiment investigated the sorption of TDCE, CDCE, BENZ and TCE, and the final experiment looked at the sorption of CLB, ODCB, MDCB and PCE. The test solutions were all prepared by adding each of the neat (or pure) organics directly to well water taken from a deep water well (in Enfield, New Hampshire) in a glass bottle, stirring for approximately three days, and then diluting if needed with additional groundwater to achieve the desired concentrations. There was no headspace in these solutions. Forty mg/L HgCl_2 was added to the test solutions to prevent biodegradation of the organics. In the first experiment the initial concentrations were approximately 40 ppb for the three nitrotoluenes and 20 ppb for the other eight compounds. In the second experiment the initial concentrations were approximately 20 ppb for BENZ, 25 ppb for CDCE and TCE, and 10 ppb for TDCE, and in the final experiment the initial concentrations were approximately 22 ppb. In the last two experiments, sampling times were the same as those in the ppm study: 1 hour, 8 hours, 24 hours (1 day), 72 hours (3 days), 168 hours (1 week) and approximately 1000 hours (6 weeks). In the first experiment, no samples were taken until 24 hours, but an additional sample was taken at approximately 500 hours (3 weeks). The early times were eliminated because these compounds had been so slowly sorbed in the previous study.

Analytical determinations for the first and third experiments were performed using reversed-phase

HPLC (RP-HPLC). For each sample a small aliquot was transferred to an autosampler vial (1.8 mL), which was filled so there was no headspace and then capped. In the third experiment a large sample loop was used; the autosampler could not be used with the large loop, so the samples were withdrawn from the autosampler vials using a 5-mL syringe and then manually injected into the HPLC.

In the first experiment a modular system was employed that consisted of a Spectra Physics 8800 ternary pump, a Dynatech LC-241 autosampler with a 100- μL loop injector, a Spectra Physics 100 variable-wavelength UV detector set at 254 nm, a Hewlett-Packard 3393A digital integrator and a Linear model 555 strip-chart recorder. Separations were obtained on a 25-cm \times 4.6-mm (5- μm) LC-18 column (Supelco) eluted with 50/50 (v/v) methanol/water at 1.5 mL/min. The detector response was obtained from the digital integrator operating in the peak height mode for all analytes except HMX, ONT, PNT and MNT. For those compounds the detector response was determined by manually measuring peak heights. This was done to improve precision.

In the third experiment a modular system was employed consisting of a Spectra Physics SP8810 isocratic pump, a Spectra Physics SP8490 variable-wavelength UV detector set at 215 nm, a Hewlett Packard 3396 series II digital integrator and a Linear model 555 strip-chart recorder. Separations were obtained on a 3.3-cm \times 4.6-mm (3- μm) LC-18 column (Supelco) preceded by an LC-8 guard column and eluted with 2.0 mL/min of 45/55 (V/V) methanol/water. A 500- μL injection loop was used for the 1, 8, 24 and 72 hour samples. A 1000- μL injection loop was used for the 168- and 1000-hour samples. The detector response was obtained by manually measuring peak heights for the 1-, 8- and 24-hour samples and from the digital integrator operating in the peak height mode for the remaining samples. Again, this was done to improve the precision of these analyses.

In the second experiment, analyses were by headspace gas chromatography. An aliquot was poured from the larger test vials into a 20-mL glass vial used for volatile organic analysis (VOA) so there was no headspace and capped. Five milliliters were then removed with a syringe from each vial, and the vials were shaken and given time for the headspace to reach equilibrium prior to analyses. Analysis was on a Photovac GC (model 10S10) equipped with a photoionization detector. Separation was achieved by injecting 250 μL of head-

space vapor onto a 10-cm-long column (0.32-cm OD) of 10% SE-30 on Chromosorb 80/100 mesh. The carrier gas was zero-grade air flowing at 20 mL/min. All chromatography was performed at

room temperature. The detector response was recorded using a strip-chart recorder (Linear Instruments), and peak heights were measured manually.

Table 2. Mean normalized* concentrations of the organics in the first experiment exposed to four well casings with time (\pm standard deviations).

| Analyte | Treatment | 24 hr | 72 hr | 168 hr | 500 hr | 1000 hr |
|---------|-----------|------------------|-------------------------------|------------------------------|------------------------------|-------------------------------|
| HMX | PTFE | 0.98 \pm 0.04 | 1.02 \pm 0.006 | 0.99 \pm 0.04 | 1.02 \pm 0.11 | 1.01 \pm 0.16 |
| | PVC | 1.02 \pm 0.008 | 1.02 \pm 0.02 | 0.98 \pm 0.03 | 0.98 \pm 0.10 | 1.00 \pm 0.12 |
| | SS 304 | 1.00 \pm 0.02 | 1.04 \pm 0.02 | 0.99 \pm 0.02 | 1.02 \pm 0.12 | 0.93 \pm 0.05 |
| | SS 316 | 1.02 \pm 0.02 | 1.04 \pm 0.03 | 1.03 \pm 0.03 | 1.00 \pm 0.11 | 1.01 \pm 0.14 |
| RDX | PTFE | 0.99 \pm 0.04 | 1.00 \pm 0.02 | 1.00 \pm 0.01 | 1.00 \pm 0.01 | 0.98 \pm 0.02 |
| | PVC | 0.99 \pm 0.02 | 0.99 \pm 0.01 | 1.00 \pm 0.01 | 1.01 \pm 0.03 | 1.00 \pm 0.03 |
| | SS 304 | 1.00 \pm 0.02 | 0.99 \pm 0.02 | 0.98 \pm 0.01 | 1.00 \pm 0.02 | 0.99 \pm 0.05 |
| | SS 316 | 1.02 \pm 0.02 | 0.98 \pm 0.02 | 0.98 \pm 0.01 | 1.00 \pm 0.01 | 0.98 \pm 0.04 |
| TNB | PTFE | 1.00 \pm 0.005 | 1.01 \pm 0.02 | 1.00 \pm 0.008 | 1.02 \pm 0.01 | 1.00 \pm 0.02 |
| | PVC | 0.99 \pm 0.02 | 1.00 \pm 0.01 | 1.00 \pm 0.01 | 1.01 \pm 0.02 | 1.02 \pm 0.01 |
| | SS 304 | 0.99 \pm 0.005 | 1.00 \pm 0.02 | 0.95 \pm 0.09 | 1.02 \pm 0.01 | 1.00 \pm 0.006 |
| | SS 316 | 0.98 \pm 0.02 | 0.99 \pm 0.02 | 1.00 \pm 0.005 | 1.02 \pm 0.01 | 0.99 \pm 0.02 |
| DNB | PTFE | 1.02 \pm 0.01 | 1.00 \pm 0.01 | 0.99 \pm 0.005 | 1.00 \pm 0.01 | 1.00 \pm 0.02 |
| | PVC | 1.02 \pm 0.01 | 1.00 \pm 0.01 | 0.98 \pm 0.01 | 0.99 \pm 0.01 | 1.01 \pm 0.01 |
| | SS 304 | 1.02 \pm 0.01 | 1.00 \pm 0.02 | 0.99 \pm 0.008 | 0.99 \pm 0.03 | 1.00 \pm 0.02 |
| | SS 316 | 1.00 \pm 0.006 | 1.00 \pm 0.03 | 0.99 \pm 0.01 | 1.00 \pm 0.02 | 1.00 \pm 0.02 |
| NB | PTFE | 0.98 \pm 0.02 | 1.00 \pm 0.01 | 0.96 \pm 0.02 | 0.99 \pm 0.02 | 0.94 [†] \pm 0.005 |
| | PVC | 0.99 \pm 0.02 | 0.98 \pm 0.01 | 0.96 \pm 0.02 | 0.99 \pm 0.01 | 0.93 [†] \pm 0.005 |
| | SS 304 | 0.98 \pm 0.02 | 1.00 \pm 0.01 | 0.98 \pm 0.01 | 0.99 \pm 0.06 | 0.98 \pm 0.01 |
| | SS 316 | 0.98 \pm 0.04 | 1.01 \pm 0.01 | 0.96 \pm 0.04 | 0.99 \pm 0.02 | 0.96 \pm 0.04 |
| TNT | PTFE | 0.99 \pm 0.005 | 0.99 \pm 0.01 | 0.99 \pm 0.02 | 1.00 \pm 0.02 | 0.85 ^{††} \pm 0.22 |
| | PVC | 0.99 \pm 0.02 | 0.99 \pm 0.02 | 0.98 \pm 0.03 | 0.98 \pm 0.01 | 0.92 \pm 0.03 |
| | SS 304 | 0.99 \pm 0.01 | 1.01 \pm 0.02 | 0.99 \pm 0.02 | 0.98 \pm 0.02 | 0.94 \pm 0.02 |
| | SS 316 | 0.98 \pm 0.006 | 0.93 ^{**} \pm 0.04 | 0.97 \pm 0.02 | 0.98 \pm 0.02 | 0.96 \pm 0.03 |
| 2AmDNT | PTFE | 1.00 \pm 0.01 | 1.00 \pm 0.02 | 0.99 \pm 0.01 | 1.00 \pm 0.03 | 0.97 \pm 0.03 |
| | PVC | 0.98 \pm 0.02 | 1.00 \pm 0.02 | 0.98 \pm 0.05 | 1.00 \pm 0.02 | 1.00 \pm 0.03 |
| | SS 304 | 1.00 \pm 0.02 | 1.00 \pm 0.04 | 0.99 \pm 0.02 | 1.00 \pm 0.02 | 0.98 \pm 0.02 |
| | SS 316 | 0.97 \pm 0.005 | 0.96 \pm 0.04 | 0.98 \pm 0.03 | 0.98 \pm 0.02 | 0.96 \pm 0.04 |
| DNT | PTFE | 0.99 \pm 0.01 | 0.99 \pm 0.02 | 0.99 \pm 0.01 | 0.99 \pm 0.02 | 0.97 \pm 0.02 |
| | PVC | 0.99 \pm 0.01 | 0.99 \pm 0.03 | 1.01 \pm 0.04 | 1.00 \pm 0.04 | 1.00 \pm 0.03 |
| | SS 304 | 1.00 \pm 0.01 | 1.00 \pm 0.04 | 1.01 \pm 0.03 | 1.01 \pm 0.04 | 1.00 \pm 0.02 |
| | SS 316 | 0.98 \pm 0.01 | 0.98 \pm 0.04 | 1.01 \pm 0.04 | 1.00 \pm 0.02 | 0.99 \pm 0.02 |
| ONT | PTFE | 0.98 \pm 0.01 | 0.97 \pm 0.05 | 0.99 \pm 0.01 | 0.94 [†] \pm 0.02 | 0.91 [†] \pm 0.02 |
| | PVC | 0.98 \pm 0.01 | 1.00 \pm 0.04 | 0.99 \pm 0.02 | 0.95 [†] \pm 0.03 | 0.92 [†] \pm 0.02 |
| | SS 304 | 0.99 \pm 0.01 | 0.99 \pm 0.04 | 1.01 \pm 0.02 | 0.98 \pm 0.02 | 0.96 \pm 0.02 |
| | SS 316 | 0.98 \pm 0.01 | 0.99 \pm 0.06 | 1.01 \pm 0.01 | 0.97 \pm 0.000 | 0.96 \pm 0.03 |
| PNT | PTFE | 1.00 \pm 0.02 | 0.99 \pm 0.05 | 0.98 \pm 0.04 | 0.92 \pm 0.01 | 0.90 [†] \pm 0.03 |
| | PVC | 0.99 \pm 0.02 | 0.96 \pm 0.04 | 0.97 \pm 0.03 | 0.92 \pm 0.03 | 0.91 [†] \pm 0.02 |
| | SS 304 | 1.00 \pm 0.02 | 0.98 \pm 0.04 | 1.00 \pm 0.02 | 0.97 \pm 0.03 | 0.99 \pm 0.02 |
| | SS 316 | 0.99 \pm 0.01 | 0.99 \pm 0.07 | 0.99 \pm 0.04 | 0.97 \pm 0.02 | 0.97 \pm 0.01 |
| MNT | PTFE | 0.99 \pm 0.02 | 0.99 \pm 0.05 | 0.93 [†] \pm 0.01 | 0.92 [†] \pm 0.02 | 0.90 [†] \pm 0.02 |
| | PVC | 0.99 \pm 0.02 | 0.98 \pm 0.02 | 0.95 \pm 0.02 | 0.95 [†] \pm 0.01 | 0.91 [†] \pm 0.02 |
| | SS 304 | 1.00 \pm 0.01 | 0.98 \pm 0.02 | 0.98 \pm 0.02 | 0.99 \pm 0.02 | 0.98 \pm 0.08 |
| | SS 316 | 0.98 \pm 0.005 | 1.00 \pm 0.07 | 0.98 \pm 0.02 | 0.98 \pm 0.02 | 0.97 \pm 0.005 |

* These values are determined by dividing the concentration of a given analyte at a given time and for a particular well casing by the mean concentration (for the same analyte) of the control samples taken at the same time and then taking the mean of these four values.

† Values significantly different from control values.

** Mean becomes 0.98 if lowest value is thrown out.

†† Mean becomes 0.98 \pm 0.015 if lowest value is thrown out.

RESULTS AND DISCUSSION

The results from the three experiments are shown in Appendix A. Tables 2, 3 and 4 present the mean normalized values for solutions exposed to the four casing materials and their standard deviations. These normalized values were obtained for each compound by dividing the mean concentra-

tion obtained for a solution exposed to one material by the mean concentration obtained for the control. There were no significant losses of any compounds exposed to stainless steel. When losses occurred with the polymers, they were generally significantly greater for PTFE than for PVC. Figure 1 presents the normalized aqueous concentration of TCE exposed to the four materials with

Table 3. Mean normalized* concentrations of the organics in the second experiment exposed to four well casings with time (\pm standard deviations).

| Analyte | Treatment | 1 hr | 8 hr | 24 hr | 72 hr | 168 hr | 1000 hr |
|---------|-----------|------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| CDCE | PTFE | 1.00 \pm 0.02 | 0.98 \pm 0.02 | 0.93 \pm 0.05 | 0.94 \pm 0.03 | 0.89 [†] \pm 0.01 | 0.79 [†] \pm 0.02 |
| | PVC | 1.00 \pm 0.006 | 0.98 \pm 0.02 | 0.96 \pm 0.03 | 0.97 \pm 0.05 | 0.94 [†] \pm 0.03 | 0.90 [†] \pm 0.05 |
| | SS 304 | 0.99 \pm 0.015 | 0.99 \pm 0.02 | 0.98 \pm 0.01 | 1.01 \pm 0.02 | 1.00 \pm 0.01 | 1.03 \pm 0.05 |
| | SS 316 | 0.99 \pm 0.01 | 1.00 \pm 0.02 | 0.98 \pm 0.01 | 1.00 \pm 0.01 | 0.99 \pm 0.02 | 0.99 \pm 0.02 |
| TDCE | PTFE | 0.98 \pm 0.02 | 0.93 [†] \pm 0.01 | 0.84 [†] \pm 0.05 | 0.84 [†] \pm 0.02 | 0.68 [†] \pm 0.02 | 0.56 [†] \pm 0.02 |
| | PVC | 0.99 \pm 0.02 | 0.97 \pm 0.01 | 0.94 \pm 0.02 | 0.96 \pm 0.02 | 0.90 [†] \pm 0.03 | 0.81 [†] \pm 0.06 |
| | SS 304 | 1.00 \pm 0.01 | 0.99 \pm 0.01 | 0.98 \pm 0.000 | 1.01 \pm 0.02 | 0.98 \pm 0.04 | 1.08 \pm 0.09 |
| | SS 316 | 0.98 \pm 0.01 | 1.00 \pm 0.02 | 0.97 \pm 0.01 | 1.00 \pm 0.01 | 0.96 \pm 0.02 | 0.96 \pm 0.04 |
| BENZ | PTFE | 1.00 \pm 0.02 | 0.98 \pm 0.02 | 0.93 \pm 0.05 | 0.97 \pm 0.04 | 0.88 [†] \pm 0.02 | 0.78 [†] \pm 0.02 |
| | PVC | 1.00 \pm 0.02 | 0.98 \pm 0.02 | 0.96 \pm 0.03 | 1.00 \pm 0.04 | 0.94 \pm 0.05 | 0.93 \pm 0.04 |
| | SS 304 | 1.00 \pm 0.006 | 0.99 \pm 0.02 | 0.98 \pm 0.02 | 1.02 \pm 0.02 | 1.00 \pm 0.02 | 1.03 \pm 0.03 |
| | SS 316 | 0.99 \pm 0.02 | 1.00 \pm 0.03 | 0.98 \pm 0.01 | 1.01 \pm 0.02 | 0.97 \pm 0.00 | 60.99 \pm 0.02 |
| TCE | PTFE | 0.99 \pm 0.03 | 0.92 [†] \pm 0.01 | 0.82 [†] \pm 0.04 | 0.80 [†] \pm 0.02 | 0.60 [†] \pm 0.02 | 0.37 [†] \pm 0.02 |
| | PVC | 1.00 \pm 0.02 | 0.97 \pm 0.03 | 0.95 \pm 0.03 | 0.97 \pm 0.03 | 0.89 [†] \pm 0.05 | 0.85 [†] \pm 0.07 |
| | SS 304 | 0.99 \pm 0.006 | 0.97 \pm 0.04 | 0.98 \pm 0.02 | 1.03 \pm 0.02 | 0.99 \pm 0.03 | 1.07 \pm 0.06 |
| | SS 316 | 0.98 \pm 0.02 | 1.00 \pm 0.02 | 0.98 \pm 0.04 | 1.00 \pm 0.04 | 0.96 \pm 0.02 | 0.98 \pm 0.04 |

* These values are determined by dividing the concentration of a given analyte at a given time and for a particular well casing by the mean concentration (for the same analyte) of the control samples taken at the same time and then taking the mean of the three replicates values.

† Values significantly different from control values.

Table 4. Mean normalized* concentrations of the organics in the third experiment exposed to four well casings with time (\pm standard deviations).

| Analyte | Treatment | 1 hr | 8 hr | 24 hr | 72 hr | 168 hr | 1000 hr |
|---------|-----------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| CLB | PTFE | 0.95 \pm 0.04 | 0.94 \pm 0.01 | 0.93 \pm 0.05 | 0.84 \pm 0.08 | 0.75 \pm 0.006 | 0.44 \pm 0.02 |
| | PVC | 0.97 \pm 0.007 | 0.98 \pm 0.04 | 0.97 \pm 0.01 | 0.93 \pm 0.02 | 0.91 \pm 0.01 | 0.77 \pm 0.03 |
| | SS 304 | 0.99 \pm 0.01 | 0.99 \pm 0.006 | 1.01 \pm 0.04 | 1.06 \pm 0.07 | 1.02 \pm 0.00 | 0.102 \pm 0.04 |
| | SS 316 | 1.01 \pm 0.007 | 0.98 \pm 0.04 | 1.00 \pm 0.05 | 1.04 \pm 0.02 | 1.01 \pm 0.03 | 1.00 \pm 0.08 |
| ODCB | PTFE | 0.93 \pm 0.004 | 0.90 [†] \pm 0.02 | 0.86 [†] \pm 0.06 | 0.73 [†] \pm 0.06 | 0.69 [†] \pm 0.01 | 0.37 [†] \pm 0.02 |
| | PVC | 0.94 \pm 0.01 | 0.99 \pm 0.02 | 0.90 [†] \pm 0.03 | 0.91 \pm 0.10 | 0.89 [†] \pm 0.02 | 0.73 [†] \pm 0.04 |
| | SS 304 | 0.98 \pm 0.006 | 0.95 \pm 0.03 | 0.95 \pm 0.04 | 0.95 \pm 0.01 | 1.03 \pm 0.01 | 0.98 \pm 0.04 |
| | SS 316 | 0.98 \pm 0.05 | 0.98 \pm 0.02 | 0.91 \pm 0.03 | 0.96 \pm 0.04 | 1.01 \pm 0.01 | 1.00 \pm 0.05 |
| MDCB | PTFE | 0.92 [†] \pm 0.05 | 0.87 [†] \pm 0.02 | 0.77 [†] \pm 0.02 | 0.61 [†] \pm 0.04 | 0.48 [†] \pm 0.02 | 0.21 [†] \pm 0.03 |
| | PVC | 0.97 \pm 0.008 | 0.96 \pm 0.000 | 0.90 \pm 0.01 | 0.77 [†] \pm 0.07 | 0.84 [†] \pm 0.09 | 0.58 [†] \pm 0.03 |
| | SS 304 | 1.00 \pm 0.000 | 0.99 \pm 0.04 | 0.97 \pm 0.01 | 0.92 \pm 0.05 | 1.02 \pm 0.02 | 1.00 \pm 0.07 |
| | SS 316 | 1.03 \pm 0.007 | 1.00 \pm 0.02 | 0.97 \pm 0.04 | 0.99 \pm 0.07 | 0.98 \pm 0.05 | 0.98 \pm 0.08 |
| PCE | PTFE | 0.89 \pm 0.08 | 0.81 [†] \pm 0.02 | 0.66 [†] \pm 0.03 | 0.51 [†] \pm 0.04 | 0.34 [†] \pm 0.01 | 0.14 [†] \pm 0.04 |
| | PVC | 0.97 \pm 0.04 | 0.96 \pm 0.04 | 0.97 \pm 0.03 | 0.91 \pm 0.04 | 0.95 \pm 0.06 | 0.76 [†] \pm 0.02 |
| | SS 304 | 1.00 \pm 0.000 | 1.00 \pm 0.04 | 0.98 \pm 0.05 | 0.93 \pm 0.02 | 1.04 \pm 0.01 | 0.97 \pm 0.08 |
| | SS 316 | 0.98 \pm 0.03 | 0.95 \pm 0.03 | 1.00 \pm 0.10 | 0.99 \pm 0.02 | 0.99 \pm 0.05 | 0.98 \pm 0.13 |

* These values are determined by dividing the concentration of a given analyte at a given time and for a particular well casing by the mean concentration (for the same analyte) of the control samples taken at the same time and then taking the mean of the three replicates values.

† Values significantly different from control values.

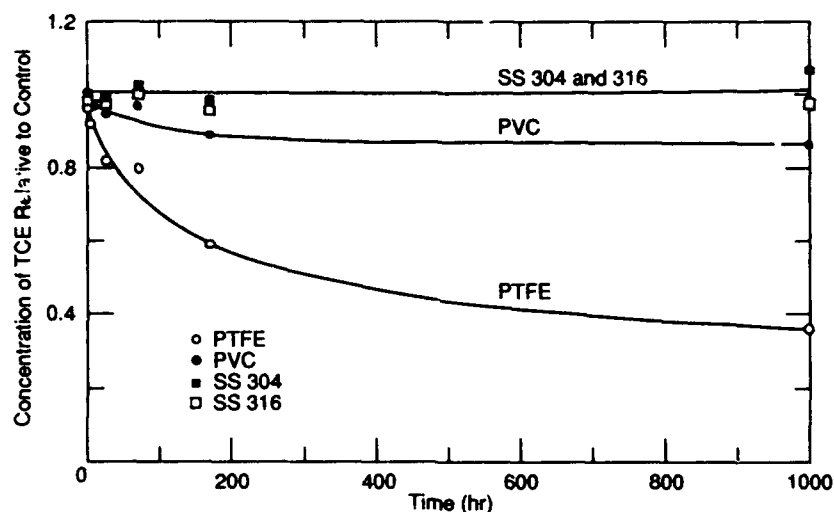


Figure 1. TCE concentrations with time when exposed to SS 304, SS 316, PVC and PTFE well casings.

time, and its behavior is typical of other analytes where losses were found. These results are similar to our previous findings (Parker et al. 1990) and those of Gillham and O'Hannesin (1990). Analysis of Variance (ANOVA) tests and Duncan's Multiple Range tests revealed that with time the differences between PVC and PTFE became significantly different (at the 95% confidence level) for eight compounds (CDCE, TDCE, TCE, PCE, BENZ, CLB, MDCB and ODCB). While losses were not significantly different between PVC and PTFE for four other compounds (NB, ONT, PNT and MNT), losses of these compounds were slight and never exceeded 10%, even after six weeks.

Of all the compounds tested, PCE was the most rapidly and extensively sorbed. This agrees well with previous findings by Reynolds and Gillham (1986). While the rate of loss we observed was not

as rapid as theirs, this difference can probably be explained by the greater surface-to-volume ratio they used and the fact that they used PTFE tubing, which is more flexible (and presumably more sorptive) than PTFE well casing.

Table 5 compares the mean normalized values for samples exposed to ppb and ppm solutions; there does not appear to be any substantial effect associated with concentration. For example, Figure 2 shows the normalized concentrations of TDCE for the ppm and ppb studies. The agreement seen here is typical for most of the compounds. Paired *t*-tests were conducted to compare the normalized values for the ppb and ppm data for each analyte (CDCE, TDCE, TCE, RDX, TNB, MNT, CLB, ODCB and MDCB) and each material. These tests revealed that there were no significant differences attributable to concentration effects, except for

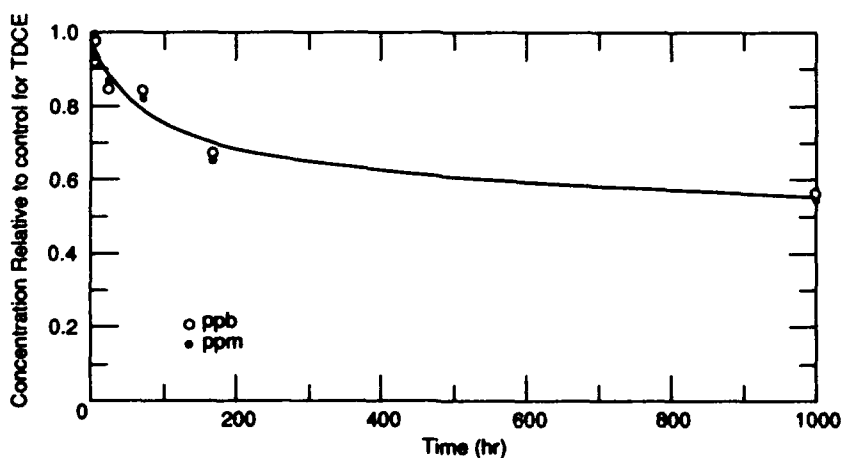


Figure 2. Comparison of TDCE data for the ppb and ppm studies.

Table 5. Comparison of mean normalized concentrations of organics between the ppb and ppm studies.

| Analyte | Treatment | 1 hr | | 8 hr | | 24 hr | | 72 hr | | 168 hr | | 1000 hr | |
|---------|-----------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|---------|-------|
| | | ppm | ppb | ppm | ppb | ppm | ppb | ppm | ppb | ppm | ppb | ppm | ppb |
| CDCE | PTFE | 1.00 | 1.01 | 0.98 | 0.96* | 0.93 | 0.96* | 0.94 | 0.94* | 0.89* | 0.91* | 0.79* | 0.79* |
| | PVC | 1.00 | 1.00 | 0.98 | 0.99 | 0.96 | 0.95 | 0.97 | 0.96 | 0.94* | 0.95 | 0.90* | 0.90 |
| | SS 304 | 0.99 | 0.97 | 0.99 | 1.00 | 0.98 | 1.00 | 1.01 | 0.96 | 1.00 | 1.04 | 1.03 | 0.98 |
| | SS 316 | 0.99 | 0.95 | 1.00 | 0.99 | 0.98 | 1.00 | 1.00 | 1.01 | 0.99 | 0.98 | 0.99 | 0.99 |
| TDCE | PTFE | 0.98 | 1.00 | 0.93* | 0.92* | 0.84* | 0.88* | 0.84* | 0.83 | 0.68* | 0.66 | 0.56* | 0.56* |
| | PVC | 0.99 | 1.00 | 0.97 | 0.98 | 0.94 | 0.93* | 0.96 | 1.06 | 0.90* | 0.83 | 0.81* | 0.83 |
| | SS 304 | 1.00 | 0.95* | 0.99 | 1.00 | 0.98 | 1.00 | 1.01 | 0.96 | 0.98 | 1.11 | 1.08 | 1.00 |
| | SS 316 | 0.98 | 1.00 | 1.00 | 0.99 | 0.97 | 1.00 | 1.00 | 1.12 | 0.96 | 1.03 | 0.96 | 1.00 |
| TCE | PTFE | 0.99 | 1.00 | 0.92* | 0.90* | 0.82* | 0.85* | 0.80* | 0.78* | 0.60* | 0.64* | 0.37* | 0.40* |
| | PVC | 1.00 | 1.01 | 0.97 | 0.98 | 0.95 | 0.94* | 0.97 | 0.99 | 0.89* | 0.94* | 0.85* | 0.88* |
| | SS 304 | 0.99 | 0.96 | 0.97 | 1.00 | 0.98 | 1.01 | 1.03 | 0.96 | 0.99 | 1.04 | 1.07 | 0.99 |
| | SS 316 | 0.98 | 1.00 | 1.00 | 0.99 | 0.98 | 1.00 | 1.00 | 1.04 | 0.96 | 0.98 | 0.98 | 1.00 |
| CLB | PTFE | 0.95 | 1.01 | 0.94 | 0.93* | 0.92 | 0.90* | 0.84* | 0.85* | 0.74* | 0.74* | 0.44* | 0.51* |
| | PVC | 0.97 | 1.01 | 0.98 | 0.98 | 0.96 | 0.95* | 0.93* | 0.98 | 0.91* | 0.94* | 0.77* | 0.86* |
| | SS 304 | 0.99 | 0.98 | 0.99 | 1.00 | 1.00 | 1.00 | 1.06 | 0.97 | 1.03 | 1.05 | 1.02 | 0.99 |
| | SS 316 | 1.01 | 0.99 | 0.98 | 0.99 | 1.00 | 1.01 | 1.04 | 1.04 | 1.01 | 0.98 | 1.00 | 0.99 |
| ODCB | PTFE | 0.93 | 1.01 | 0.90* | 0.91* | 0.86* | 0.88* | 0.73* | 0.81* | 0.69* | 0.68* | 0.37* | 0.43* |
| | PVC | 0.94 | 1.02 | 0.99 | 0.97* | 0.90* | 0.94* | 0.91 | 0.98 | 0.89* | 0.93 | 0.73* | 0.86* |
| | SS 304 | 0.98 | 0.98 | 0.95 | 0.99 | 0.95 | 1.00 | 0.95 | 0.99 | 1.03 | 1.04 | 0.98 | 1.00 |
| | SS 316 | 0.98 | 1.01 | 0.98 | 0.98 | 0.91 | 1.01 | 0.96 | 1.03 | 1.01 | 0.98 | 1.00 | 1.00 |
| MDCB | PTFE | 0.92* | 1.00 | 0.87* | 0.84* | 0.77* | 0.78* | 0.61* | 0.66* | 0.48* | 0.48* | 0.21* | 0.26* |
| | PVC | 0.97 | 1.02 | 0.96 | 0.95* | 0.90 | 0.92* | 0.77* | 0.97 | 0.84* | 0.88* | 0.58* | 0.80* |
| | SS 304 | 1.00 | 0.99 | 0.99 | 0.96* | 0.97 | 1.00 | 0.92 | 0.99 | 1.02 | 1.02 | 1.00 | 1.02 |
| | SS 316 | 1.03 | 1.03 | 1.00 | 0.96* | 0.97 | 1.00 | 0.99 | 1.04 | 0.98 | 0.96 | 0.98 | 1.01 |
| RDX | PTFE | | | | | 0.99 | 1.00 | 1.00 | 1.02 | 1.00 | 0.91 | 0.98 | 0.99 |
| | PVC | | | | | 0.99 | 0.98 | 0.99 | 1.00 | 1.00 | 1.02 | 1.00 | 1.00 |
| | SS 304 | | | | | 1.00 | 1.01 | 0.99 | 1.02 | 0.98 | 1.10 | 0.99 | 0.98 |
| | SS 316 | | | | | 1.02 | 1.01 | 0.98 | 1.02 | 0.98 | 1.11 | 0.98 | 1.00 |
| TNB | PTFE | | | | | 1.00 | 1.00 | 1.01 | 0.98 | 1.00 | 0.95 | 1.00 | 1.01 |
| | PVC | | | | | 0.99 | 0.98 | 1.00 | 1.02 | 1.00 | 1.01 | 1.02 | 1.02 |
| | SS 304 | | | | | 0.99 | 1.00 | 1.00 | 1.05 | 0.95 | 1.07 | 1.00 | 1.00 |
| | SS 316 | | | | | 0.98 | 1.01 | 0.99 | 1.07 | 1.00 | 1.06 | 0.99 | 1.02 |
| MNT | PTFE | | | | | 0.99 | 0.99 | 0.99 | 0.99 | 0.93* | 0.90 | 0.90* | 0.90* |
| | PVC | | | | | 0.99 | 0.98 | 0.98 | 1.05 | 0.95 | 0.99 | 0.91* | 0.94 |
| | SS 304 | | | | | 1.00 | 1.01 | 0.98 | 1.00 | 0.98 | 1.08 | 0.98 | 1.07 |
| | SS 316 | | | | | 0.98 | 1.02 | 1.00 | 1.08 | 0.98 | 1.10 | 0.97 | 0.99 |

* Values significantly different from controls.

TCE and TNB exposed to SS 316, and ODCB exposed to SS 304 and PVC. In these cases, normalized concentrations were significantly lower for the ppb data. For the compounds exposed to the SS 316, this difference may be an artifact resulting from the analyses in the ppm study where the normalized values for SS 316 were greater than 1.00.

We performed regression analyses on the final normalized concentrations of samples exposed to PVC and PTFE vs the corresponding aqueous solubilities, molecular weights and log K_{ow} values. As we saw in the ppm study, there was a statistically significant relationship between the log K_{ow} and only the final normalized concentration (Fig. 3). This inverse relationship was statistically significant at the 99% confidence level for

both the PVC and PTFE data (correlation coefficient = -0.77 and -0.70, respectively). Thus, the higher the K_{ow} , the greater the loss.

Using partitioning as a model, we (Parker et al. 1990) modeled the loss of organics from solution by PTFE by first assuming that sorption was reversible. Thus

$$C_{aq} \xrightleftharpoons[k_2]{k_1} C_{sorb}$$

where C_{aq} = concentration of analyte in aqueous solution

C_{sorb} = concentration of analyte sorbed by the plastic

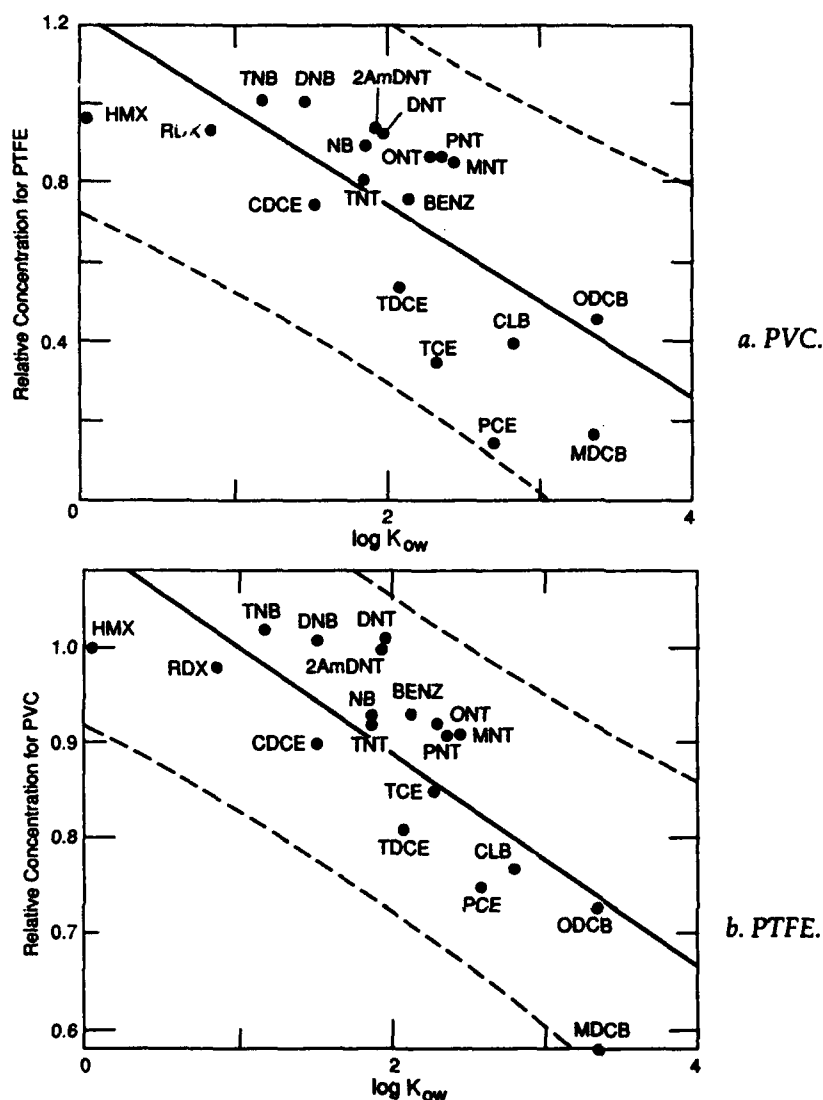


Figure 3. Regression of the relative concentrations vs $\log K_{ow}$

k_1 and k_2 = first-order rate constants for sorption and desorption, respectively.

We can then write the rate equation as (Gould 1959):

$$\frac{d[C_{aq}]}{dt} = -k_1[C_{aq}] + k_2[C_{sorb}]. \quad (2)$$

Since the volume of the solution was ten times that of the polymeric material,

$$[C_{sorb}] = 10([C_0] - [C_{aq}]) \quad (3)$$

where $[C_0]$ is the initial concentration of the analyte in solution. If we substitute back into the rate equation (eq 2) and regroup terms, we get:

$$\frac{d[C_{aq}]}{dt} = -(k_1 + 10k_2)[C_{aq}] + 10k_2[C_0]. \quad (4)$$

Since k_1 , k_2 and C_0 are constants, this can be rewritten as:

$$\frac{d[C_{aq}]}{dt} = -A[C_{aq}] + B \quad (5)$$

where

$$A = k_1 + 10k_2 \quad (6)$$

and

$$B = 10k_2[C_0]. \quad (7)$$

If the rate equation is then integrated, we have a nonlinear relation for $[C_{aq}]$ as a function of t and two constants A and B :

$$\frac{-\ln(A[C_{aq}] + B)}{A} = t. \quad (8)$$

The optimal values for A and B for each analyte where sorption was observed can be obtained by applying the Gauss-Newton method of nonlinear curve fitting using the normalized concentrations at 1, 8, 24, 72, 128 and 1000 hours. Then using these values we can solve for k_1 and k_2 . The ratio of k_1/k_2 is the equilibrium constant, K_{eq} .

Table 6. Rate and equilibrium constants for the ppm and ppb studies for sorption into PTFE.

| Analyte | ppm study | | ppb study | |
|---------|--|----------|--|----------|
| | k_1/k_2 | k_{eq} | k_1/k_2 | k_{eq} |
| CDCE | $\frac{8.4 \times 10^{-4}}{3.12 \times 10^{-4}} = 2.7$ | | $\frac{1.08 \times 10^{-3}}{4.12 \times 10^{-4}} = 2.6$ | |
| TDCE | $\frac{3.79 \times 10^{-3}}{4.85 \times 10^{-4}} = 7.8$ | | $\frac{3.69 \times 10^{-3}}{4.84 \times 10^{-4}} = 7.6$ | |
| TCE | $\frac{3.84 \times 10^{-3}}{2.64 \times 10^{-4}} = 14.5$ | | $\frac{4.04 \times 10^{-3}}{2.41 \times 10^{-4}} = 16.8$ | |
| CLB | $\frac{2.47 \times 10^{-3}}{2.57 \times 10^{-4}} = 9.6$ | | $\frac{2.21 \times 10^{-3}}{1.68 \times 10^{-4}} = 16.1$ | |
| ODCB | $\frac{3.17 \times 10^{-3}}{2.42 \times 10^{-4}} = 13.1$ | | $\frac{3.58 \times 10^{-3}}{2.22 \times 10^{-4}} = 31.1$ | |
| MDCB | $\frac{6.78 \times 10^{-3}}{2.68 \times 10^{-4}} = 25.3$ | | $\frac{7.09 \times 10^{-3}}{2.28 \times 10^{-4}} = 31.1$ | |
| PDCB | $\frac{7.46 \times 10^{-3}}{3.04 \times 10^{-4}} = 24.5$ | | — | |
| PCE | — | | $\frac{1.30 \times 10^{-2}}{3.52 \times 10^{-4}} = 36.9$ | |
| BENZ | — | | $\frac{9.6 \times 10^{-4}}{3.35 \times 10^{-4}} = 2.9$ | |
| MNT | $\frac{7.1 \times 10^{-4}}{5.96 \times 10^{-4}} = 1.2$ | | $\frac{4.6 \times 10^{-4}}{4.23 \times 10^{-4}} = 1.1$ | |
| PNT | — | | $\frac{2.0 \times 10^{-4}}{1.3 \times 10^{-4}} = 1.5$ | |

Table 6 gives the values for k_1 , k_2 and K_{eq} for both the ppm data (Parker et al. 1990) and ppb data for PTFE. Given that concentrations in the ppm study were approximately 100 times those in the ppb study, there is reasonably good agreement between the rate constants for sorption and desorption and the equilibrium coefficient (k_1 , k_2 and K_{eq}) for the two studies for the six analytes where loss was observed. The reason the k_1 , k_2 and K_{eq} values for the ppm study do not agree with those published previously (Parker et al. 1990) is because these values were derived using the measured concentration rather than the normalized concentration. Any losses due to absorption by the Teflon liners in the cap or adsorption by the glass container are removed from the estimates of k_1 and k_2 by using the normalized concentrations. Also, A was incorrectly defined as $k_1 + k_2$ in Parker et al. (1990) rather than $k_1 + 10k_2$ (eq 6). As we saw in the previous study, those compounds showing the most rapid sorption (k_1) are not necessarily those that are the most readily desorbed (k_2). In the present study, k_1 is greatest for PCE, while k_2 is greatest for TDCE.

In the previous study we (Parker et al. 1990) found that we could predict K_{eq} in PTFE from the $\log K_{ow}$ for most of the compounds we tested but that this relationship overestimated losses for compounds subject to hydrogen bonding. When we conducted a similar regression on our ppb data, we found a similar relationship, where K_{eq} increased with increasing $\log K_{ow}$ for nine of the ten compounds where we were able to derive K_{eq} using the Gauss-Newton method of nonlinear curve fitting. For PCE, sorption was much greater than would be predicted based on $\log K_{ow}$. This relationship was not statistically significant at the 95% confidence level, but it was when the value for PCE was removed from the analysis. We recognize that the octanol-water model is deficient in explaining the interaction of solutes with these (organic) polymer surfaces. Preliminary analysis of these data using a linear solvation energy model (LSER), which treats the interactions in terms of specific, physically meaningful components, shows considerable promise. However, since modeling was not the primary focus of this paper, that work will be presented later (Leggett and Parker, in prep.).

While we conclude that concentration has no effect on the rate constants for sorption by polymers at ppm and ppb levels, this would not be the case for high concentrations (approaching solubility) of solvents in polymers subject to swelling,

such as rigid PVC (but not PTFE). According to several researchers (Berens 1985, Jenkins et al. 1986, Holsen 1988) diffusion of an organic through a glassy polymer (e.g. PVC) depends on the compound's activity and its ability to swell the polymer. For an aqueous solution, the activity of an organic can be approximated by:

$$a = C/C_s \quad (9)$$

where a = activity

C = concentration of the organic in water

C_s = solubility of the organic in water.

The Flory-Huggins interaction parameter (χ) can be used as a measure of the ability of a solvent to swell a glassy polymer (Berens 1985). This parameter is related to the activity (a) as follows:

$$\ln(a) = \ln(V_1) + (1 - V_1) + (1 - V_1)^2 \chi \quad (10)$$

where V_1 is the volume fraction of solvent in the polymer. In general, if χ is less than 0.5, the solvent will completely dissolve the polymer (Berens 1985). For values greater than 0.5, the larger the number, the less the swelling power.

At the lowest activities, diffusion will be purely Fickian and thus concentration independent and slowest (Berens 1985, Jenkins et al. 1986, Holsen 1988). At higher activities, diffusion becomes successively concentration dependent, then anomalous, and finally Case II, and the rate of diffusion increases several orders of magnitude (Berens 1985,

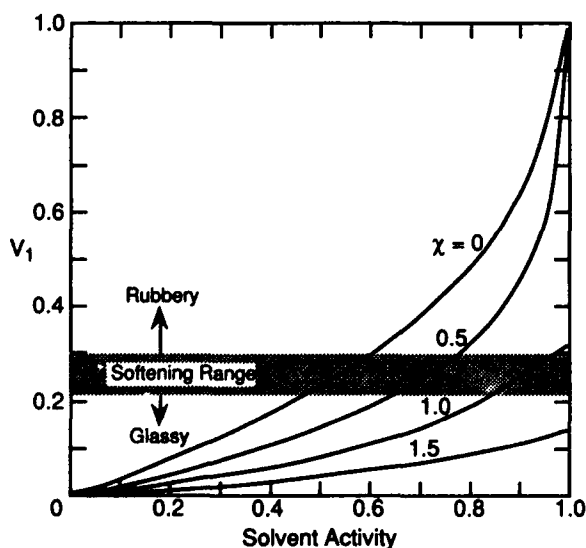


Figure 4. Mole volume fraction of solvent in PVE vs solvent activity for various χ values. (After Berens 1985.)

Jenkins et al. 1986, Holsen 1988). The greater the ability of the organic permeant to swell the polymer, the lower will be the activity required to move from purely Fickian to other diffusion mechanisms.

There is some disagreement regarding which activities will soften rigid PVC. According to Berens (1985), rigid PVC will be softened only by strong solvents or swelling agents ($\chi = 0$) at activities greater than 0.5. For less aggressive solvents, even higher activities are needed (Fig. 4). Berens predicted that diffusion of an organic in aqueous solution in PVC pipe will be Fickian if the activity is less than 0.25. However, Vonk (1985, 1986) felt that while diffusion would be Fickian for poorer PVC solvents (e.g. alkylated aromatics) at activities less than 0.25, the activity should be less than 0.1 for better solvents (e.g. anilines, chlorinated hydrocarbons, ketones and nitrobenzenes). The activities of the solutions used in our study were all well below even the lowest limit (0.1); the highest activity was 0.05 for RDX. Thus, we would expect these solutions to behave like typical dilute solutions where diffusion is independent of concentration.

CONCLUSIONS AND RECOMMENDATIONS

In almost all instances, there was no effect of concentration on the percent loss relative to the controls at these low levels (ppm and ppb). These results support the conclusion that for PVC and PTFE, the organics in solution behave like typical dilute solutions, that absorption involving partitioning and dissolution into the polymer matrix has occurred, and that diffusion is independent of concentration. For stainless steel there were no losses due to sorption.

PTFE sorbs PCE more rapidly than any other compound tested to date. For this compound we observed a 10% loss in less than 1 hour and a 34% loss in 24 hours. While it is hard to extrapolate the results of laboratory findings to a monitoring situation, the rate of sorption (k_1) of some compounds by PTFE may be rapid enough to be of concern when monitoring groundwater. While there are losses associated with rigid PVC, the rate and extent of loss does not appear to be large enough to be of concern when monitoring groundwater. In instances where sorptive losses of organics by PTFE are of concern, it might be better to use PVC or stainless steel casings. The alternative is to allow adequate time for equilibration between PTFE and

well water; our data indicate that approximately two weeks should be adequate.

Thus, from this and previous studies (Reynolds and Gillham 1986, Gillham and O'Hannesin 1990, Parker et al. 1990, Reynolds et al. 1990), we conclude that there is no basis for preferentially using stainless steel or PTFE casings over PVC casings when monitoring for low levels of organics. If one expects to find very high concentrations of a PVC solvent (with concentrations approaching solubility) or pure product (of a PVC solvent), then PVC should not be used. However, when monitoring for metals, several studies by Hewitt (Parker et al. 1990, Hewitt 1992, Hewitt, in press) indicate that stainless steel should not be used. Hewitt found that stainless steel (304 and 316) screens can leach and sorb significant quantities of several metals rapidly enough so that analyte concentrations are affected even under dynamic conditions (Hewitt, in press). Thus, selection of a casing should depend on the types and concentrations of expected analytes and the characteristics of the site.

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APPENDIX A: RESULTS FROM THE THREE EXPERIMENTS

Table A1. Concentration (µg/L) in samples from the first experiment.

| Sample | | HMX | RDX | TNB | DNB | NB | TNT | 2AmDNT | DNT | ONT | PNT | MNT |
|--------------------|-----------|------|------|------|------|------|------|--------|------|------|------|------|
| a. After 24 hours. | | | | | | | | | | | | |
| Control | 1 | 20.2 | 20.3 | 19.7 | 19.2 | 19.8 | 19.3 | 19.8 | 19.7 | 37.8 | 38.8 | 39.3 |
| | 2 | 20.3 | 20.2 | 20.3 | 20.2 | 19.8 | 19.8 | 20.2 | 19.9 | 40.0 | 41.5 | 40.1 |
| | 3 | 19.8 | 20.0 | 20.2 | 20.6 | 20.4 | 19.6 | 20.9 | 20.4 | 38.8 | 40.3 | 40.2 |
| | 4 | 19.8 | 20.0 | 20.3 | 20.1 | 20.5 | 19.5 | 20.5 | 19.6 | 39.7 | 40.2 | 38.7 |
| | \bar{x} | 20.0 | 20.1 | 20.1 | 20.0 | 20.1 | 19.6 | 20.4 | 19.9 | 39.1 | 40.2 | 39.6 |
| PTFE | 1 | 20.0 | 19.0 | 20.2 | 20.2 | 20.0 | 19.4 | 20.3 | 19.5 | 38.5 | 39.5 | 38.5 |
| | 2 | 18.7 | 19.7 | 19.8 | 20.1 | 19.8 | 19.2 | 20.1 | 19.9 | 38.7 | 39.8 | 40.0 |
| | 3 | 20.1 | 20.4 | 20.1 | 20.5 | 19.7 | 19.5 | 20.4 | 20.0 | 37.8 | 40.8 | 39.4 |
| | 4 | 20.2 | 20.7 | 20.0 | 20.3 | 19.2 | 19.4 | 20.5 | 19.8 | 38.9 | 40.2 | 39.2 |
| | \bar{x} | 19.8 | 20.0 | 20.0 | 20.3 | 19.7 | 19.4 | 20.3 | 19.8 | 38.5 | 40.1 | 39.3 |
| PVC | 1 | 20.6 | 19.7 | 19.9 | 20.0 | 20.0 | 18.8 | 19.6 | 19.6 | 38.8 | 39.7 | 39.9 |
| | 2 | 20.4 | 20.4 | 19.2 | 20.5 | 20.0 | 19.5 | 20.0 | 19.6 | 37.7 | 39.0 | 38.5 |
| | 3 | 20.2 | 20.0 | 20.3 | 20.3 | 19.7 | 20.0 | 20.5 | 19.9 | 38.2 | 40.5 | 39.7 |
| | 4 | 20.5 | 19.4 | 20.3 | 20.5 | 19.5 | 19.6 | 20.1 | 20.0 | 38.7 | 40.2 | 39.0 |
| | \bar{x} | 20.4 | 19.9 | 19.9 | 20.3 | 19.8 | 19.5 | 20.0 | 19.8 | 38.4 | 39.8 | 39.3 |
| SS 304 | 1 | 20.0 | 20.4 | 19.9 | 19.9 | 19.3 | 19.2 | 20.2 | 19.5 | 38.3 | 39.9 | 39.7 |
| | 2 | 19.5 | 20.4 | 19.8 | 20.5 | 19.6 | 19.4 | 20.3 | 20.1 | 38.2 | 39.8 | 40.2 |
| | 3 | 20.4 | 20.6 | 19.8 | 20.2 | 20.4 | 19.6 | 20.1 | 19.9 | 38.6 | 40.7 | 39.2 |
| | 4 | 19.5 | 20.5 | 20.2 | 20.3 | 19.9 | 19.7 | 20.8 | 20.1 | 38.9 | 40.8 | 39.3 |
| | \bar{x} | 19.8 | 20.5 | 19.9 | 20.2 | 19.8 | 19.5 | 20.4 | 19.9 | 38.5 | 40.3 | 39.6 |
| SS 316 | 1 | 20.7 | 20.1 | 19.8 | 20.0 | 19.8 | 19.2 | 19.7 | 19.6 | 37.4 | 39.5 | 39.0 |
| | 2 | 20.0 | 19.8 | 19.6 | 20.1 | 20.1 | 19.4 | 19.7 | 19.4 | 37.8 | 39.3 | 38.4 |
| | 3 | 20.1 | 20.5 | 19.0 | 20.0 | 20.3 | 19.5 | 19.6 | 19.8 | 38.8 | 40.0 | 38.7 |
| | 4 | 20.7 | 20.2 | 19.9 | 20.1 | 18.6 | 19.3 | 19.8 | 19.5 | 39.0 | 39.7 | 38.9 |
| | \bar{x} | 20.4 | 20.2 | 19.6 | 20.0 | 19.7 | 19.4 | 19.7 | 19.6 | 38.2 | 39.6 | 38.8 |
| b. After 72 hours. | | | | | | | | | | | | |
| Control | 1 | 19.2 | 20.2 | 19.3 | 19.5 | 19.7 | 18.9 | 19.0 | 18.6 | 37.4 | 38.3 | 37.4 |
| | 2 | 20.2 | 19.7 | 20.1 | 19.9 | 20.2 | 19.8 | 20.1 | 20.2 | 39.3 | 41.6 | 41.6 |
| | 3 | 20.8 | 20.2 | 20.7 | 19.9 | 20.8 | 19.8 | 21.4 | 20.1 | 40.5 | 40.7 | 39.9 |
| | 4 | 19.9 | 20.4 | 20.9 | 20.5 | 19.8 | 20.0 | 20.8 | 20.5 | 39.0 | 40.4 | 39.6 |
| | \bar{x} | 20.0 | 20.1 | 20.2 | 20.0 | 20.1 | 19.6 | 20.3 | 19.9 | 39.0 | 40.2 | 39.6 |
| PTFE | 1 | 20.6 | 19.2 | 20.0 | 19.8 | 20.0 | 19.2 | 20.0 | 19.2 | 37.2 | 38.4 | 38.4 |
| | 2 | 20.3 | 20.3 | 20.5 | 19.9 | 20.0 | 19.4 | 20.0 | 19.7 | 40.3 | 42.6 | 42.1 |
| | 3 | 20.4 | 20.3 | 20.8 | 20.0 | 20.5 | 19.7 | 20.8 | 19.9 | 36.0 | 39.0 | 38.7 |
| | 4 | 20.5 | 20.2 | 20.6 | 20.3 | 20.4 | 19.5 | 20.7 | 20.0 | 38.8 | 39.3 | 38.0 |
| | \bar{x} | 20.4 | 20.0 | 20.5 | 20.0 | 20.2 | 19.4 | 20.4 | 19.7 | 38.1 | 39.8 | 39.3 |
| PVC | 1 | 20.2 | 19.8 | 20.2 | 19.9 | 20.2 | 19.4 | 19.8 | 19.1 | 37.2 | 37.1 | 38.6 |
| | 2 | 20.2 | 19.4 | 20.2 | 19.8 | 19.6 | 19.1 | 20.1 | 19.4 | 39.6 | 38.0 | 38.0 |
| | 3 | 19.9 | 20.1 | 20.2 | 20.0 | 19.4 | 19.3 | 20.6 | 19.9 | 39.8 | 39.2 | 38.4 |
| | 4 | 20.9 | 20.1 | 20.7 | 20.3 | 19.4 | 19.7 | 20.7 | 20.3 | 40.0 | 40.5 | 39.9 |
| | \bar{x} | 20.3 | 19.8 | 20.3 | 20.0 | 19.6 | 19.4 | 20.3 | 19.7 | 39.2 | 38.7 | 38.7 |
| SS 304 | 1 | 20.4 | 20.2 | 19.6 | 19.6 | 20.1 | 19.2 | 19.1 | 18.8 | 37.0 | 36.8 | 37.8 |
| | 2 | 21.0 | 19.4 | 20.2 | 20.1 | 20.2 | 19.6 | 20.3 | 20.1 | 39.3 | 39.4 | 38.5 |
| | 3 | 20.3 | 20.1 | 20.6 | 20.3 | 20.7 | 20.2 | 21.2 | 20.4 | 37.4 | 39.9 | 38.7 |
| | 4 | 21.3 | 20.0 | 20.7 | 19.9 | 20.4 | 19.7 | 20.4 | 20.2 | 40.4 | 40.7 | 39.8 |
| | \bar{x} | 20.8 | 19.9 | 20.3 | 20.0 | 20.4 | 19.7 | 20.2 | 19.9 | 38.5 | 39.2 | 38.7 |
| SS 316 | 1 | 20.4 | 19.0 | 19.6 | 19.0 | 19.6 | 18.0 | 18.4 | 18.4 | 37.4 | 37.8 | 37.2 |
| | 2 | 20.4 | 19.7 | 19.7 | 19.7 | 20.1 | 19.1 | 20.3 | 19.7 | 41.7 | 43.6 | 43.4 |
| | 3 | 21.6 | 19.6 | 20.5 | 20.2 | 20.1 | 17.3 | 19.7 | 20.0 | 36.6 | 39.8 | 38.9 |
| | 4 | 20.6 | 20.0 | 20.2 | 20.6 | 20.2 | 18.8 | 19.5 | 19.9 | 38.8 | 37.9 | 39.0 |
| | \bar{x} | 20.8 | 19.6 | 20.0 | 20.0 | 20.0 | 18.3 | 19.5 | 19.5 | 38.6 | 39.8 | 39.6 |

Table A1 (cont'd). Concentration ($\mu\text{g/L}$) in samples from the first experiment.

| Sample | | HMX | RDX | TNB | DNB | NB | TNT | 2AmDNT | DNT | ONT | PNT | MNT |
|---------------------|-----------|------|------|------|------|------|------|--------|------|------|------|------|
| c. After 168 hours. | | | | | | | | | | | | |
| Control | 1 | 20.1 | 20.4 | 19.8 | 19.8 | 19.6 | 18.6 | 19.6 | 19.4 | 39.1 | 40.2 | 38.9 |
| | 2 | 19.7 | 20.1 | 20.4 | 20.2 | 19.8 | 19.5 | 20.0 | 20.2 | 39.8 | 41.8 | 40.7 |
| | 3 | 19.9 | 19.8 | 20.3 | 20.2 | 21.0 | 19.6 | 19.5 | 19.9 | 39.4 | 41.0 | 40.3 |
| | 4 | 20.2 | 19.8 | 20.3 | 19.9 | 20.2 | 20.7 | 22.0 | 20.0 | 38.1 | 38.5 | 38.2 |
| | \bar{x} | 20.0 | 20.0 | 20.2 | 20.0 | 20.1 | 19.6 | 20.3 | 19.9 | 39.1 | 40.4 | 39.5 |
| PTFE | 1 | 20.1 | 20.2 | 20.2 | 19.8 | 19.5 | 19.1 | 20.0 | 19.7 | 38.4 | 38.5 | 36.7 |
| | 2 | 20.1 | 20.1 | 20.4 | 19.7 | 19.5 | 19.5 | 19.8 | 19.9 | 39.1 | 39.4 | 37.1 |
| | 3 | 20.1 | 19.7 | 19.5 | 19.8 | 18.8 | 19.7 | 20.5 | 20.0 | 38.8 | 42.2 | 37.4 |
| | 4 | 18.5 | 20.0 | 20.2 | 19.6 | 19.4 | 19.3 | 20.0 | 19.6 | 39.1 | 38.1 | 36.0 |
| | \bar{x} | 19.7 | 20.0 | 20.1 | 19.7 | 19.3 | 19.4 | 20.1 | 19.8 | 38.9 | 39.6 | 36.8 |
| PVC | 1 | 19.6 | 20.1 | 20.0 | 19.3 | 19.3 | 18.9 | 19.4 | 19.6 | 38.4 | 37.7 | 36.7 |
| | 2 | 20.0 | 19.9 | 20.5 | 19.7 | 19.7 | 19.1 | 19.7 | 19.8 | 39.4 | 37.7 | 38.2 |
| | 3 | 19.8 | 20.0 | 20.5 | 19.8 | 18.6 | 19.2 | 19.1 | 19.9 | 39.4 | 40.2 | 38.2 |
| | 4 | 18.8 | 19.6 | 20.2 | 19.6 | 19.3 | 19.9 | 21.3 | 21.2 | 37.7 | 39.8 | 38.2 |
| | \bar{x} | 19.6 | 19.9 | 20.3 | 19.6 | 19.2 | 19.3 | 19.9 | 20.1 | 38.7 | 38.8 | 37.8 |
| SS 304 | 1 | 19.1 | 19.6 | 16.3 | 19.7 | 19.5 | 19.2 | 19.9 | 19.8 | 39.1 | 39.4 | 38.2 |
| | 2 | 19.9 | 19.7 | 20.2 | 19.9 | 19.8 | 19.0 | 19.6 | 19.6 | 40.1 | 39.8 | 38.9 |
| | 3 | 20.0 | 19.8 | 20.1 | 19.6 | 19.4 | 19.4 | 19.7 | 19.9 | 40.1 | 41.4 | 40.0 |
| | 4 | 19.9 | 19.3 | 19.9 | 19.7 | 19.7 | 19.9 | 20.8 | 20.9 | 38.8 | 39.4 | 38.2 |
| | \bar{x} | 19.7 | 19.6 | 19.1 | 19.7 | 19.6 | 19.4 | 20.0 | 20.0 | 39.5 | 40.0 | 38.8 |
| SS 316 | 1 | 21.4 | 19.9 | 20.1 | 19.7 | 19.9 | 18.8 | 19.4 | 19.4 | 38.8 | 39.4 | 38.9 |
| | 2 | 20.0 | 19.6 | 20.1 | 19.9 | 19.4 | 18.8 | 20.3 | 20.9 | 39.4 | 41.8 | 39.6 |
| | 3 | 20.8 | 19.9 | 20.3 | 20.0 | 19.8 | 19.7 | 20.4 | 20.1 | 39.8 | 38.5 | 38.9 |
| | 4 | 20.2 | 19.8 | 20.0 | 19.4 | 18.3 | 18.9 | 19.1 | 19.5 | 39.8 | 39.4 | 38.2 |
| | \bar{x} | 20.6 | 19.8 | 20.1 | 19.8 | 19.4 | 19.0 | 19.8 | 20.0 | 39.4 | 39.8 | 38.9 |
| d. After 500 hours. | | | | | | | | | | | | |
| Control | 1 | 17.6 | 19.6 | 19.8 | 19.5 | 20.1 | 17.8 | 19.5 | 19.2 | 38.5 | 39.4 | 38.6 |
| | 2 | - | 19.6 | 20.4 | 19.8 | 20.5 | 19.9 | 20.4 | 19.7 | 39.1 | 40.2 | 39.6 |
| | 3 | 21.8 | 20.6 | 20.4 | 20.3 | 18.9 | 20.4 | 20.8 | 20.3 | 39.7 | 40.6 | 40.0 |
| | 4 | 20.7 | 20.7 | 20.2 | 20.5 | 20.1 | 20.4 | 20.6 | 20.2 | 39.1 | 40.6 | 40.3 |
| | \bar{x} | 20.0 | 20.1 | 20.2 | 20.0 | 20.0 | 19.6 | 20.3 | 19.8 | 39.1 | 40.2 | 39.6 |
| PTFE | 1 | 17.8 | 20.4 | 20.5 | 19.9 | 20.0 | 19.9 | 19.7 | 19.5 | 35.9 | 37.5 | 36.1 |
| | 2 | - | 19.8 | 20.4 | 19.8 | 19.4 | 19.0 | 19.8 | 19.4 | 36.2 | 36.7 | 36.1 |
| | 3 | 21.2 | 20.4 | 20.8 | 20.3 | 20.1 | 19.7 | 20.3 | 19.9 | 37.2 | 36.7 | 36.8 |
| | 4 | 21.9 | 20.2 | 20.8 | 19.7 | 20.1 | 19.7 | 21.0 | 20.3 | 37.2 | 37.5 | 37.1 |
| | \bar{x} | 20.3 | 20.2 | 20.6 | 19.9 | 19.9 | 19.6 | 20.2 | 19.8 | 36.6 | 37.1 | 36.5 |
| PVC | 1 | 17.3 | 19.8 | 20.3 | 19.5 | 19.7 | 19.2 | 20.5 | 19.3 | 35.6 | 35.2 | 37.1 |
| | 2 | - | 20.1 | 20.4 | 19.7 | 19.9 | 18.9 | 19.6 | 19.4 | 38.1 | 36.7 | 37.5 |
| | 3 | 21.1 | 20.1 | 19.9 | 19.8 | 20.1 | 19.1 | 20.3 | 19.9 | 38.1 | 37.9 | 37.8 |
| | 4 | 20.8 | 21.3 | 20.9 | 20.1 | 19.7 | 19.4 | 20.9 | 21.1 | 37.5 | 38.3 | 38.2 |
| | \bar{x} | 19.7 | 20.3 | 20.4 | 19.8 | 19.8 | 19.2 | 20.3 | 19.9 | 37.3 | 37.0 | 37.6 |
| SS 304 | 1 | 17.6 | 19.6 | 20.1 | 19.3 | 18.0 | 18.8 | 19.8 | 19.6 | 37.8 | 37.5 | 38.2 |
| | 2 | - | 20.5 | 20.6 | 20.2 | 20.4 | 19.3 | 19.8 | 19.8 | 38.8 | 39.0 | 39.3 |
| | 3 | 21.9 | 20.3 | 20.8 | 20.4 | 20.3 | 19.4 | 20.9 | 21.3 | 39.1 | 39.8 | 39.6 |
| | 4 | 21.5 | 20.2 | 20.8 | 19.3 | 21.1 | 19.7 | 20.5 | 20.0 | 37.8 | 39.8 | 40.0 |
| | \bar{x} | 20.3 | 20.2 | 20.6 | 19.8 | 20.0 | 19.3 | 20.2 | 20.2 | 38.4 | 39.0 | 39.3 |
| SS 316 | 1 | 17.8 | 19.9 | 20.3 | 19.5 | 20.0 | 18.6 | 20.0 | 19.5 | 38.1 | 39.0 | 39.3 |
| | 2 | - | 20.2 | 20.7 | 19.9 | 19.3 | 19.5 | 19.8 | 19.7 | 37.8 | 38.3 | 39.3 |
| | 3 | 20.4 | 20.1 | 20.6 | 20.1 | 20.3 | 19.4 | 19.2 | 19.6 | 37.8 | 38.3 | 38.2 |
| | 4 | 21.9 | 20.6 | 20.6 | 20.3 | 20.1 | 19.6 | 20.0 | 20.5 | 37.8 | 40.2 | 39.3 |
| | \bar{x} | 20.0 | 20.2 | 20.6 | 20.0 | 19.9 | 19.3 | 19.8 | 19.8 | 37.9 | 39.0 | 39.0 |

Table A1 (cont'd).

| Sample | | HMX | RDX | TNB | DNB | NB | TNT | 2AmDNT | DNT | ONT | PNT | MNT |
|----------------------|-----------|------|------|------|------|------|-------|--------|------|------|------|------|
| e. After 1000 hours. | | | | | | | | | | | | |
| Control | 1 | 16.8 | 20.9 | 20.3 | 19.5 | 20.1 | 19.3 | 20.1 | 20.2 | 39.4 | 40.8 | 39.7 |
| | 2 | 19.6 | 20.2 | 20.7 | 20.1 | 19.9 | 20.0 | 20.4 | 19.9 | 39.7 | 39.9 | 39.7 |
| | 3 | 23.6 | 19.7 | 19.7 | 19.9 | 19.7 | 19.8 | 20.3 | 20.0 | 39.0 | 40.3 | 38.6 |
| | 4 | 19.9 | 19.8 | 20.4 | 20.0 | 20.5 | 19.3 | 20.4 | 19.5 | 38.4 | 39.5 | 40.1 |
| | \bar{x} | 20.0 | 20.1 | 20.3 | 19.9 | 20.0 | 19.6 | 20.3 | 19.9 | 39.1 | 40.1 | 39.5 |
| PTFE | 1 | 17.0 | 19.7 | 19.6 | 19.8 | 18.9 | 18.6 | 20.1 | 19.7 | 35.8 | 37.9 | 36.1 |
| | 2 | 22.6 | 20.1 | 20.2 | 19.8 | 18.9 | 19.2 | 20.4 | 19.4 | 36.7 | 36.7 | 36.1 |
| | 3 | 23.5 | 19.0 | 20.7 | 20.2 | 18.6 | 18.9 | 19.7 | 19.5 | 35.4 | 36.3 | 35.4 |
| | 4 | 17.8 | 19.5 | 20.0 | 20.4 | 18.9 | 10.1* | 18.9 | 18.9 | 34.4 | 35.0 | 34.3 |
| | \bar{x} | 20.2 | 19.6 | 20.1 | 20.0 | 18.8 | 16.7† | 19.8 | 19.4 | 35.6 | 36.5 | 35.5 |
| PVC | 1 | 16.9 | 19.8 | 20.5 | 20.0 | 18.6 | 17.6 | 19.5 | 19.4 | 35.8 | 35.9 | 35.7 |
| | 2 | 21.5 | 19.2 | 20.8 | 19.9 | 18.7 | 18.6 | 20.3 | 20.2 | 35.1 | 35.9 | 37.2 |
| | 3 | 22.2 | 20.6 | 20.8 | 20.3 | 18.6 | 17.4 | 20.0 | 19.6 | 35.4 | 37.5 | 35.4 |
| | 4 | 19.6 | 20.6 | 20.5 | 20.1 | 18.5 | 18.3 | 21.1 | 20.7 | 36.7 | 37.5 | 35.7 |
| | \bar{x} | 20.0 | 20.0 | 20.6 | 20.1 | 18.6 | 18.0 | 20.2 | 20.0 | 35.8 | 36.7 | 36.0 |
| SS 304 | 1 | 17.3 | 20.7 | 20.0 | 20.0 | 19.5 | 18.0 | 20.0 | 20.1 | 37.7 | 39.5 | 38.6 |
| | 2 | 18.5 | 18.4 | 19.9 | 19.4 | 20.1 | 18.4 | 20.2 | 20.2 | 37.1 | 39.9 | 39.4 |
| | 3 | 19.6 | 20.1 | 20.1 | 19.9 | 19.8 | 18.2 | 19.4 | 19.6 | 37.4 | 40.7 | 39.0 |
| | 4 | 18.9 | 20.1 | 20.3 | 20.2 | 19.7 | 18.9 | 19.9 | 19.6 | 38.7 | 39.1 | 39.0 |
| | \bar{x} | 18.6 | 19.8 | 20.1 | 19.9 | 19.8 | 18.4 | 19.9 | 19.9 | 37.7 | 39.8 | 39.0 |
| SS 316 | 1 | 19.6 | 20.3 | 20.3 | 19.9 | 18.0 | 18.8 | 19.4 | 19.6 | 38.7 | 39.1 | 38.6 |
| | 2 | 18.5 | 20.0 | 20.0 | 19.9 | 19.7 | 18.6 | 19.7 | 19.8 | 37.1 | 39.1 | 37.9 |
| | 3 | 24.2 | 19.6 | 19.5 | 19.5 | 19.0 | 18.1 | 18.6 | 19.1 | 36.1 | 38.7 | 38.3 |
| | 4 | 18.1 | 18.5 | 20.5 | 20.5 | 20.1 | 19.6 | 20.6 | 20.2 | 38.4 | 39.9 | 38.6 |
| | \bar{x} | 20.1 | 19.6 | 20.1 | 20.0 | 19.2 | 18.8 | 19.6 | 19.7 | 37.6 | 39.2 | 38.4 |

* Repeat analysis was similar, 10.4.

† Mean of first three values is 18.9.

Table A2. Concentration (µg/L) in samples from the second experiment.

| <i>Sample</i> | <i>TDCE</i> | <i>CDCE</i> | <i>BENZ</i> | <i>TCE</i> | <i>TDCE</i> | <i>CDCE</i> | <i>BENZ</i> | <i>TCE</i> | <i>TDCE</i> | <i>CDCE</i> | <i>BENZ</i> | <i>TCE</i> |
|---------------------------|-------------|-------------|-------------|------------|---------------------------|-------------|-------------|------------|-----------------------------|-------------|-------------|------------|
| a. After 1 hour. | | | | | b. After 8 hours. | | | | c. After 24 hours. | | | |
| Control 1 | 4.73 | 17.2 | 10.4 | 15.9 | 5.20 | 19.6 | 11.4 | 18.1 | 4.73 | 17.3 | 10.2 | 15.1 |
| 2 | 4.95 | 18.1 | 10.6 | 16.2 | 5.14 | 19.5 | 11.4 | 18.0 | 4.75 | 17.8 | 10.7 | 16.3 |
| 3 | 4.76 | 17.6 | 10.7 | 16.3 | 5.14 | 19.6 | 11.4 | 17.9 | 4.73 | 18.0 | 10.9 | 16.4 |
| \bar{x} | 4.81 | 17.6 | 10.6 | 16.1 | 5.16 | 19.6 | 11.4 | 18.0 | 4.74 | 17.7 | 10.6 | 15.9 |
| PTFE 1 | 4.57 | 17.1 | 10.5 | 15.5 | 4.75 | 18.8 | 10.9 | 16.3 | 3.76 | 15.5 | 9.33 | 12.4 |
| 2 | 4.78 | 17.8 | 10.6 | 16.1 | 4.81 | 19.5 | 11.2 | 16.3 | 4.08 | 16.8 | 9.97 | 13.4 |
| 3 | 4.78 | 17.8 | 10.8 | 16.3 | 4.87 | 19.5 | 11.3 | 16.8 | 4.19 | 17.2 | 10.24 | 13.6 |
| \bar{x} | 4.71 | 17.6 | 10.6 | 16.0 | 4.81 | 19.3 | 11.1 | 16.5 | 4.01 | 16.5 | 9.85 | 13.1 |
| PVC 1 | 4.73 | 17.6 | 10.7 | 16.2 | 5.08 | 19.6 | 11.4 | 18.0 | 4.35 | 16.5 | 9.88 | 14.5 |
| 2 | 4.84 | 17.8 | 10.4 | 15.8 | 5.05 | 19.4 | 11.2 | 17.4 | 4.57 | 17.5 | 10.52 | 15.4 |
| 3 | 4.78 | 17.6 | 10.7 | 16.2 | 4.96 | 19.0 | 10.9 | 16.9 | 4.49 | 17.1 | 10.29 | 15.3 |
| \bar{x} | 4.78 | 17.7 | 10.6 | 16.1 | 5.03 | 19.3 | 11.2 | 17.4 | 4.47 | 17.0 | 10.2 | 15.1 |
| SS 304 1 | 4.87 | 17.8 | 10.6 | 16.1 | 5.17 | 19.7 | 11.3 | 16.8 | 4.65 | 17.1 | 10.2 | 15.3 |
| 2 | 4.81 | 17.3 | 10.5 | 16.0 | 5.05 | 19.3 | 11.1 | 17.4 | 4.67 | 17.6 | 10.5 | 15.8 |
| 3 | 4.78 | 17.4 | 10.5 | 15.9 | 5.17 | 19.7 | 11.5 | 18.1 | 4.67 | 17.6 | 10.4 | 15.9 |
| \bar{x} | 4.82 | 17.5 | 10.5 | 16.0 | 5.13 | 19.6 | 11.3 | 17.4 | 4.66 | 17.4 | 10.4 | 15.7 |
| SS 316 1 | 4.72 | 17.4 | 10.4 | 15.6 | 5.20 | 19.7 | 11.4 | 18.0 | 4.62 | 17.1 | 10.1 | 15.3 |
| 2 | 4.68 | 17.3 | 10.3 | 15.4 | 4.99 | 19.2 | 11.1 | 17.4 | 4.65 | 17.6 | 10.5 | 15.9 |
| 3 | 4.78 | 17.6 | 10.7 | 16.4 | 5.23 | 20.0 | 11.6 | 18.3 | 4.57 | 17.2 | 10.5 | 15.7 |
| \bar{x} | 4.73 | 17.4 | 10.5 | 15.8 | 5.14 | 19.6 | 11.4 | 17.9 | 4.61 | 17.3 | 10.4 | 15.6 |
| d. After 72 hours. | | | | | e. After 168 hours | | | | f. After 1000 hours. | | | |
| Control 1 | 4.84 | 18.0 | 10.2 | 14.5 | 3.78 | 15.5 | 9.13 | 14.6 | 2.87 | 15.0 | 8.64 | 11.4 |
| 2 | 4.74 | 17.9 | 10.2 | 14.8 | 3.56 | 15.1 | 8.92 | 13.4 | 3.10 | 14.7 | 8.43 | 12.1 |
| 3 | 4.68 | 17.5 | 10.1 | 14.8 | 3.85 | 16.0 | 9.56 | 14.9 | 2.79 | 14.5 | 8.47 | 11.1 |
| \bar{x} | 4.75 | 17.8 | 10.2 | 14.7 | 3.73 | 15.5 | 9.20 | 14.3 | 2.92 | 14.7 | 8.51 | 11.5 |
| PTFE 1 | 4.00 | 16.3 | 9.80 | 11.7 | 2.47 | 13.7 | 7.96 | 8.39 | 1.64 | 11.5 | 6.67 | 4.16 |
| 2 | 4.08 | 17.4 | 10.29 | 12.1 | 2.63 | 14.0 | 8.22 | 8.79 | 1.57 | 11.3 | 6.51 | 4.16 |
| 3 | 3.88 | 16.6 | 9.56 | 11.3 | 2.51 | 13.9 | 8.07 | 8.32 | 1.72 | 11.9 | 6.92 | 4.62 |
| \bar{x} | 3.99 | 16.8 | 9.88 | 11.7 | 2.54 | 13.9 | 8.08 | 8.50 | 1.64 | 11.6 | 6.70 | 4.31 |
| PVC 1 | 4.49 | 16.3 | 9.80 | 13.8 | 3.31 | 14.3 | 8.49 | 12.4 | 2.55 | 13.9 | 8.35 | 10.28 |
| 2 | 4.66 | 17.9 | 10.25 | 14.5 | 3.23 | 14.4 | 8.38 | 12.1 | 2.33 | 12.9 | 7.80 | 9.31 |
| 3 | 4.61 | 17.6 | 10.54 | 14.6 | 3.48 | 15.1 | 9.08 | 13.5 | 2.20 | 12.6 | 7.64 | 8.80 |
| \bar{x} | 4.59 | 17.3 | 10.2 | 14. | 3.34 | 14.6 | 8.65 | 12.7 | 2.36 | 13.1 | 7.93 | 9.46 |
| SS 304 1 | 4.72 | 17.7 | 10.2 | 14.7 | 3.64 | 15.5 | 9.08 | 14.1 | 3.41 | 16.0 | 9.02 | 12.9 |
| 2 | 4.81 | 18.0 | 10.4 | 15.1 | 3.51 | 15.3 | 9.08 | 13.7 | 2.88 | 14.7 | 8.56 | 11.6 |
| 3 | 4.84 | 18.2 | 10.5 | 15.4 | 3.77 | 15.7 | 9.34 | 14.6 | 3.18 | 14.9 | 8.56 | 12.5 |
| \bar{x} | 4.79 | 18.0 | 10.4 | 15. | 3.64 | 15.5 | 9.17 | 14.1 | 3.16 | 15.2 | 8.71 | 12.3 |
| SS 316 1 | 4.80 | 17.8 | 10.4 | 15.1 | 3.71 | 15.5 | 9.02 | 14.1 | 2.92 | 14.7 | 8.56 | 11.7 |
| 2 | 4.75 | 17.9 | 10.4 | 15.0 | 3.51 | 15.1 | 8.92 | 13.6 | 2.79 | 14.5 | 8.47 | 11.3 |
| 3 | 4.57 | 17.6 | 10.0 | 14.0 | 3.58 | 15.4 | 8.92 | 13.6 | 2.68 | 14.3 | 8.29 | 10.8 |
| \bar{x} | 4.71 | 17.8 | 10.3 | 14.7 | 3.60 | 15.3 | 8.95 | 13.8 | 2.80 | 14.5 | 8.44 | 11.3 |

Table A3. Concentration (µg/L) in samples from the third experiment.

| Sample | CLB | ODCB | PCE | MDCB | CLB | ODCB | PCE | MDCB | CLB | ODCB | PCE | MDCB | |
|--------------------|-----------|------|------|------|---------------------|------|------|------|----------------------|------|------|------|------|
| a. After 1 hour. | | | | | b. After 8 hours. | | | | c. After 24 hours. | | | | |
| Control | 1 | 18.8 | 19.5 | 19.5 | 19.1 | 18.4 | 20.0 | 22.2 | 21.1 | 19.1 | 20.5 | 21.8 | 20.1 |
| | 2 | — | — | — | — | 19.5 | 19.3 | 21.8 | 19.5 | 19.0 | 19.8 | 20.6 | 18.4 |
| | 3 | 19.2 | 20.1 | 20.1 | 19.3 | 19.9 | 20.4 | 22.2 | 19.5 | 17.8 | 19.8 | 17.8 | 18.0 |
| | \bar{x} | 19.0 | 19.8 | 19.8 | 19.2 | 19.3 | 19.9 | 22.1 | 20.0 | 18.6 | 20.0 | 20.1 | 18.8 |
| PTFE | 1 | 18.3 | 18.0 | 18.5 | 18.2 | 18.2 | 18.0 | 18.2 | 17.9 | 18.2 | 18.2 | 13.9 | 15.0 |
| | 2 | — | — | — | — | 18.0 | 17.6 | 18.2 | 17.5 | 16.9 | 17.6 | 12.8 | 14.2 |
| | 3 | 17.6 | 18.7 | 16.8 | 17.2 | 17.8 | 18.3 | 17.2 | 17.1 | 16.5 | 16.0 | 12.7 | 14.2 |
| | \bar{x} | 18.0 | 18.4 | 17.6 | 17.7 | 18.0 | 18.0 | 17.9 | 17.5 | 17.2 | 17.3 | 13.1 | 14.5 |
| PVC | 1 | 18.3 | 18.0 | 19.5 | 18.6 | 19.1 | 20.0 | 21.2 | 19.1 | 18.2 | 18.5 | 20.1 | 16.7 |
| | 2 | — | — | — | — | 18.2 | 19.0 | 21.2 | 19.9 | 17.8 | 17.2 | 19.5 | 17.1 |
| | 3 | 18.5 | 19.0 | 18.9 | 18.6 | 19.5 | 19.7 | 21.2 | 18.3 | 17.8 | 18.2 | 18.9 | 16.7 |
| | \bar{x} | 18.4 | 18.5 | 19.2 | 18.6 | 18.9 | 19.6 | 21.2 | 19.1 | 17.9 | 18.0 | 19.5 | 16.8 |
| SS 304 | 1 | 18.8 | 19.1 | 19.5 | 19.0 | 18.9 | 18.3 | 21.2 | 20.7 | 19.1 | 18.6 | 20.6 | 18.4 |
| | 2 | — | — | — | — | 19.1 | 19.7 | 22.8 | 19.9 | 19.0 | 19.8 | 20.1 | 18.4 |
| | 3 | 18.8 | 19.5 | 20.1 | 19.3 | 19.1 | 19.0 | 21.8 | 19.1 | 17.8 | 18.5 | 18.4 | 18.0 |
| | \bar{x} | 18.8 | 19.3 | 19.8 | 19.2 | 19.0 | 19.0 | 21.9 | 19.9 | 18.6 | 19.0 | 19.7 | 18.3 |
| SS 316 | 1 | 18.8 | 18.4 | 19.5 | 19.5 | 18.2 | 19.0 | 20.2 | 19.9 | 18.8 | 18.5 | 20.6 | 18.8 |
| | 2 | — | — | — | — | 18.9 | 19.7 | 21.8 | 19.5 | 19.3 | 18.9 | 21.8 | 18.4 |
| | 3 | 19.3 | 20.3 | 19.3 | 20.0 | 19.9 | 19.6 | 21.2 | 20.3 | 17.6 | 17.6 | 17.4 | 17.4 |
| | \bar{x} | 19.1 | 19.4 | 19.4 | 19.8 | 19.0 | 19.4 | 21.1 | 19.9 | 18.6 | 18.3 | 20.0 | 18.2 |
| d. After 72 hours. | | | | | e. After 168 hours. | | | | f. After 1000 hours. | | | | |
| Control | 1 | 16.0 | 16.9 | 15.6 | 17.1 | 15.6 | 16.4 | 12.9 | 14.9 | 14.9 | 15.7 | 11.9 | 13.0 |
| | 2 | 16.3 | 17.4 | 16.5 | 17.2 | 16.7 | 16.9 | 13.7 | 15.9 | 14.4 | 15.3 | 10.8 | 12.1 |
| | 3 | 16.5 | 16.9 | 16.6 | 17.1 | 16.3 | 16.9 | 13.4 | 16.0 | 15.5 | 16.1 | 13.1 | 14.1 |
| | \bar{x} | 16.3 | 17.1 | 16.2 | 17.1 | 16.2 | 16.7 | 13.3 | 15.6 | 14.9 | 15.7 | 11.9 | 13.1 |
| PTFE | 1 | 15.1 | 12.7 | 8.84 | 10.9 | 12.2 | 11.7 | 4.68 | 7.26 | 6.77 | 5.88 | 2.12 | 3.27 |
| | 2 | 13.5 | 11.3 | 8.06 | 9.7 | 12.0 | 11.4 | 4.53 | 7.52 | 6.24 | 5.94 | 1.68 | 2.46 |
| | 3 | 12.7 | 13.3 | 7.77 | 10.4 | 12.1 | 11.5 | 4.39 | 7.73 | 6.53 | 5.52 | 1.32 | 2.61 |
| | \bar{x} | 13.7 | 12.4 | 8.22 | 10.3 | 12.1 | 11.5 | 4.53 | 7.50 | 6.51 | 5.78 | 1.71 | 2.78 |
| PVC | 1 | 14.9 | 17.2 | 15.4 | 11.8 | 14.9 | 15.0 | 13.5 | 14.6 | 11.6 | 11.8 | 8.92 | 7.47 |
| | 2 | 15.1 | 13.9 | 14.5 | 14.2 | 14.6 | 14.6 | 12.2 | 12.0 | 11.8 | 11.6 | 9.22 | 7.99 |
| | 3 | 15.6 | 15.6 | 14.2 | 13.7 | 14.5 | 14.9 | 12.0 | 12.5 | 10.9 | 10.9 | 8.78 | 7.31 |
| | \bar{x} | 15.2 | 15.6 | 14.7 | 13.2 | 14.7 | 14.8 | 12.6 | 13.0 | 11.4 | 11.4 | 8.97 | 7.59 |
| SS 304 | 1 | 15.9 | 16.0 | 14.8 | 14.8 | 16.6 | 17.1 | 13.7 | 16.0 | 15.8 | 15.8 | 12.1 | 13.4 |
| | 2 | 17.7 | 16.0 | 15.2 | 15.9 | 16.6 | 17.3 | 13.8 | 15.6 | 15.0 | 15.7 | 12.0 | 13.7 |
| | 3 | 18.1 | 16.5 | 15.3 | 16.5 | 16.5 | 17.0 | 14.0 | 16.1 | 14.7 | 14.7 | 10.5 | 12.1 |
| | \bar{x} | 17.2 | 16.2 | 15.1 | 15.7 | 16.6 | 17.1 | 13.8 | 15.9 | 15.2 | 15.4 | 11.5 | 13.1 |
| SS 316 | 1 | 16.4 | 15.7 | 15.7 | 18.2 | 16.7 | 17.0 | 13.8 | 16.0 | 15.5 | 15.8 | 11.7 | 12.8 |
| | 2 | 17.3 | 16.4 | 16.5 | 15.8 | 15.9 | 16.7 | 12.6 | 14.5 | 15.7 | 16.3 | 13.2 | 13.7 |
| | 3 | 17.0 | 17.0 | 16.1 | 16.9 | 16.7 | 16.9 | 13.1 | 15.4 | 13.4 | 14.9 | 10.1 | 11.8 |
| | \bar{x} | 16.9 | 16.4 | 16.1 | 17.0 | 16.4 | 16.9 | 13.2 | 15.3 | 14.9 | 15.7 | 11.7 | 12.8 |

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| 13. ABSTRACT (Maximum 200 words) This report examines sorption of low ppb levels of organic solutions by polytetrafluoroethylene (PTFE), rigid polyvinyl chloride (PVC) and stainless steel 304 and 316 well casings. Nineteen organics that were either on the EPA priority pollutant list or of concern to the U.S. Army were selected, including several munitions and chlorinated solvents. These compounds were selected to give a range in physical properties such as solubility in water, octanol-water partition coefficient and molecular structure. When these results were compared with the results from a similar study conducted at ppm levels, the rate and extent of sorption by PTFE and PVC was the same for almost all analytes. There were no losses of any compounds associated with stainless steel. At these low levels (ppm and ppb) the rate of diffusion within the polymer (PVC and PTFE) is independent of concentration. Only with PTFE are the rates rapid enough to be of concern when monitoring for some compounds in groundwater. Tetrachloroethylene was the compound sorbed by PTFE the most rapidly. The study showed that PVC well casings are suitable for monitoring low levels (ppm and ppb) of organics. | | | |
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